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Catalytic abatement of nitrogen oxides–stationary applications

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Abstract

Emission regulations for unburned hydrocarbons, nitrogen oxides and particulates are becoming more stringent throughout the world. Nitrogen oxides include NO, NO_2 and N_2O. Transportation (mobile source) and fuel combustion (stationary source) are the main sources of nitrogen oxide emissions [1]. This review will update the commercial catalytic applications for abating nitrogen compounds (including nitrogen oxides) and will summarize the status of the following technologies applied to stationary source emissions: (1) selective catalytic reduction of NO_x using ammonia (SCR); (2) non-selective catalytic reduction of NO_x (NSCR); (3) nitrous oxide (N_2O) decomposition; and (4) ammonia (NH_3) decomposition.

The major sources of NO_x from stationary sources are power generation, stationary engines, industrial boilers, process heaters and gas turbines [2]. SCR is usually applied to all these sources and NSCR is applied mainly to the stationary engines. N_2O decomposition is used mainly in the chemical industry associated with nylon intermediate manufacture. NH_3 decomposition is a fairly new application and can be applied to SCR to decompose NH_3 emissions from industrial operations.
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Keywords: NO_x reduction; Ammonia; Selective catalytic reduction; V_2O_5/TiO_2; Non-selective catalytic reduction; Pt/Rh; Nitrous oxide; Co/beta zeolite

1. Selective catalytic reduction (SCR) of NO_x

Many challenges exist when applying catalysis/catalysts to fuel combustion processes (stationary applications) for NO_x emission control [3,4,5,6]. The basic chemistry involves the following reactions:

$$\left.\begin{array}{l} 4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \\ 4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \end{array}\right\}$$

selective or desired reactions

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$\left.\begin{array}{l} 4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \\ 4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \end{array}\right\}$$

non-selective reactions

Ammonia or in some cases urea reacts selectively to reduce the NO_x. The non-selective reaction consumes the reagent and reduces the NO_x conversion. In situations where sulfur compounds are present, the conversion to SO_3 must be minimized to prevent salt formation and deposits on heat transfer surfaces, which reduce the heat transfer efficiency. In mobile applications, the SO_3 must also be minimized since this leads to increased particulates.

The reaction scheme for the major SCR NH_3/NO_x reactions can be depicted in Fig. 1 [3]. The NH_3 can react selectively with the NO_x to give N_2 or react non-selectively to give N_2 or NO_x. This parallel reaction scheme results in the following characteristic diagram for SCR as shown in Fig. 2.

There have been a number of catalytic technologies investigated for use in SCR over the years and the major catalyst performance characteristics are shown

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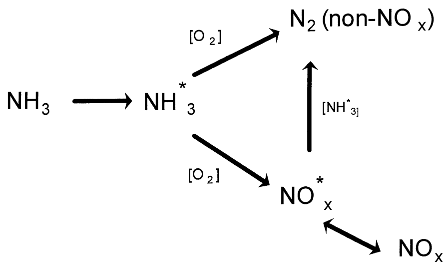

Fig. 1. Reaction schematic for SCR NO_x. From Catalytic Air Pollution Control: Commercial Technology [3].

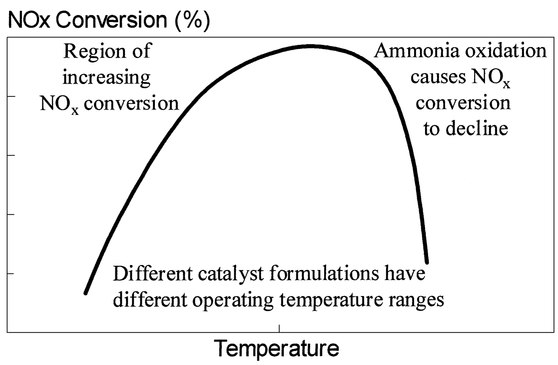

Fig. 2. Maximum peformance for SCR NO_x.

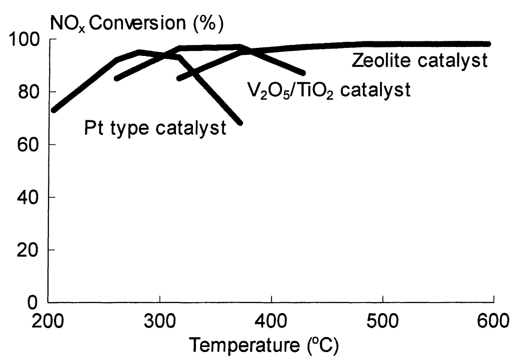

Fig. 3. Three major families of SCR catalyst [7].

in the Fig. 3 [7]. The various characteristics of these catalyst families as described by one manufacturer are given in Table 1.

In addition to operating characteristics, there are other potential side reactions in the various catalysts that impact the operation of the SCR unit and downstream equipment. These side reactions are listed in Table 2.

Table 1
Operating characteristics of different SCR catalysts

Medium temperature – VNX™ catalyst (V_2O_5/TiO_2)
500–800°F (260–425°C)
most broadly used
10–15 years of experience
sulfur tolerant
High temperature – ZNX™ catalysts (zeolite)
650–1100°F (345–590°C)
very high NO_x conversion
very low NH_3 slip
NH_3 destruction
sulfur tolerant above 800°F (425°C)
Low temperature – LT catalyst (Pt-based)
300–520°F (150–300°C)
narrow temperature window
temperature window shifts
not sulfur tolerant

Table 2
Other reactions over the SCR catalyst affect performance

Reaction/comments	Condition
Oxidation of NH_3	high temperature
uses NH_3	extremely low NO_x
increases NO_x	
Nitrous oxide (N_2O) formation	type of catalyst
	absence of moisture
Nitrite/nitrate salt formation	low temperature
explosive	
Ammonium (bi)sulfate condensation	catalyst composition
plugging	SO_2 oxidation to SO_3
particulates	low temperature

The majority of commercial installations use the V_2O_5/TiO_2 either as extruded monoliths or deposited on a plate structure although, there are a number of installations that use a zeolite technology. The level of the V_2O_5 is important and must be controlled to minimize the SO_3 formation [8]. Additionally, modifiers such as Mo and W are added to minimize SO_3 formation. One manufacturer even claims that adding the W improves long-term performance [8]. Sulfur poisoning of the V_2O_5/TiO_2 does not appear to be a major issue in commercial applications.

Major catalyst poisons in coal-fired applications are Na, K and As while in applications where lubricating oils are present, such as stationary engines and gas turbines, the P from ZDP compounds can deactivate the catalyst. Still, the coal fired SCR catalyst life is

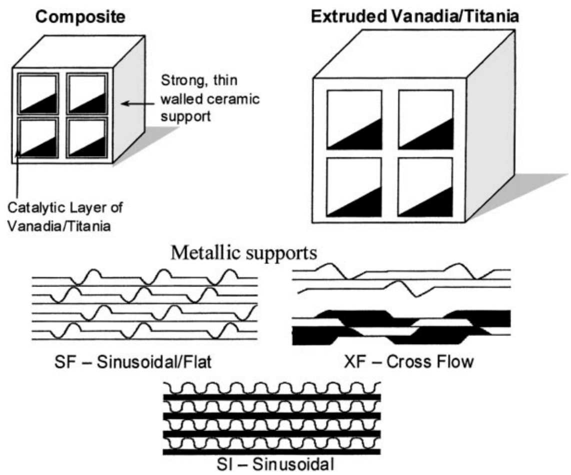

Fig. 4. Many alternatives exist for SCR NO_x catalysts depending on application.

projected to be about nine years [9]. In all applications of the V_2O_5/TiO_2 technology, excessively high temperatures are a design issue since the anatase (high surface area) form of the Ti converts to rutile (low surface area) causing irreversible deactivation.

Listed below are several applications for SCR NO_x:

- Gas fired utility boilers
- Coal fired boilers
- Oil fired boilers
- Process heaters
- Gas turbines
- Stationary engines
- Nitric acid plants
- Steel mills
- Chemical plants

Because of the variant exhaust gas compositions, particulate loading and contaminants, there are different catalyst support structures as shown in Fig. 4. The extruded catalyst and the metallic support are typically used in high dust conditions and have low cell densities (10–100 cells/in.^{2} or cpsi) and the composite catalyst (either on a metallic or ceramic monolith) is used in low dust conditions and has a higher cell density (from 64 to 400 cpsi).

A typical installation for a SCR NO_x unit is shown in the following schematic Fig. 5. Note that the critical design parameters are the location of the SCR reactor structure and the design of the ammonia injection grid. The mixing of the ammonia must be uniform to

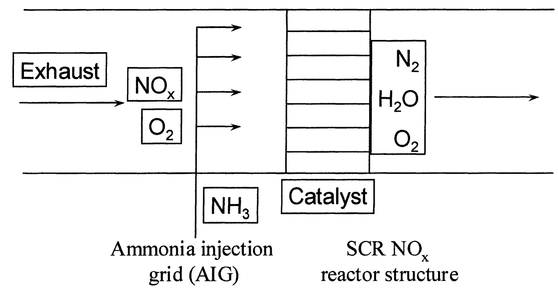

Fig. 5. Major equipment in SCR design.

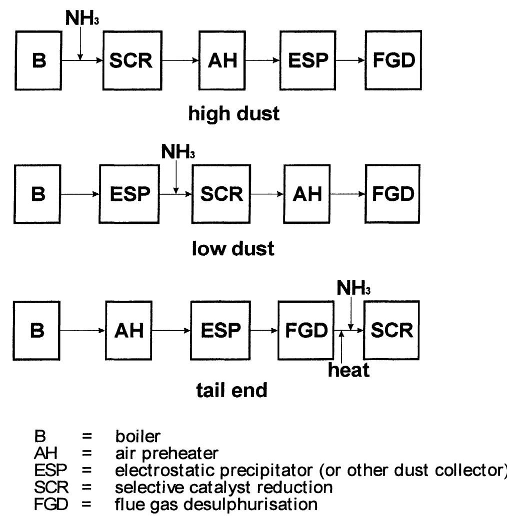

Fig. 6. Design options for SCR in coal fired boilers. Published by permission of Institute of Clean Air Companies (ICAC).

assure a set NH_3/NO_x ratio which will then dictate the amount of NO_x removal.

There are a number of design options for SCR installations in coal fired utility boilers as shown in Fig. 6 [9].

In the ‘high dust’ configuration, particulate levels can vary between 1 and 30 g/m^3 depending on the type of boiler and the quality of the fuel. In the ‘low dust’ and ‘tail end’ configuration, particulate levels are much lower, typically $<$100 mg/m^3. Since levels of dust or particulates vary, the honeycomb geometry and catalyst preparation method can change for each location. For instance, in the high dust location, extruded catalyst or plate type of low cell density may be used while in the tail end application, a high cell density may be specified. Most of the other applications

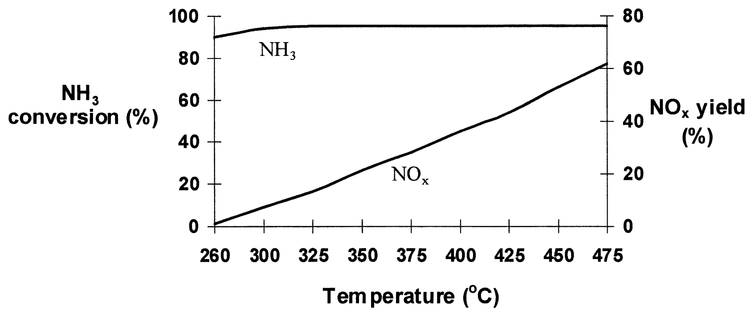

Fig. 7. Ammonia destruction possible after SCR catalyst.

for SCR have low dust or particulate loadings and use high cell density supports.

One interesting new technology addresses the unconverted NH_3 in the SCR reactions. In most applications, the NH_3 slip or NH_3 in the exhaust is also specified or regulated along with the NO_x emissions. An NH_3 destruction catalyst is now being offered for reducing the NH_3 emissions after the SCR installation. The performance of this catalyst technology is shown in Fig. 7.

SCR NO_x is a fairly mature technology for stationary applications and little changes are anticipated beyond process design improvements and expanded use of the high temperature catalyst technology. The next major application may be in mobile applications such as diesel trucks and some lean burn gasoline engines where hydrocarbons derived from the fuel are not effective reductants. Also, the vanadia-based SCR technology is effective in the abatement of dioxins from waste incineration plants [8].

2. Non-selective catalytic reduction (NSCR) of NO_x

NSCR NO_x is derived from automotive catalysis [3]. The basic reaction chemistry occurs in a rich atmosphere and the oxygen content of the exhaust is reduced so that three-way catalysis (TWC) can occur. The reactions are as follows:

Deplete oxygen:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$UHC + O_2 \rightarrow CO_2 + H_2O$$

Convert NO_x:

$$NO_x + CO \rightarrow CO_2 + N_2$$

$$NO_x + H_2 \rightarrow H_2O + N_2$$

$$NO_x + UHC \rightarrow CO_2 + H_2O + N_2$$

The typical catalyst technology is Pt/Rh derived from automotive catalyst technology. Most of the commercial installations use either ceramic or metallic honeycomb supports. The majority of applications are in nitric acid plants and stationary engines. This is a mature business and the expected catalyst life is ∼10 years. Catalyst deactivation does occur from ash deposits from the lubricating oil and in rare cases from thermal sintering. Typical performance of this technology on a natural gas stationary engine is given in Fig. 8.

3. Nitrous oxide (N_2O) decomposition

In the manufacture of nylon, the intermediate chemical synthesis produces large quantities of N_2O as a byproduct. The emissions from this specific chemical process are regulated and a catalytic decomposition technology has been developed to address this need. N_2O is a greenhouse gas with long-term stability. This reaction is a strict decomposition as follows:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$

Many different catalytic materials have been investigated and both the support and catalytic component prove critical for the decomposition at lower operating temperature [10]. The performance of a Co/Beta zeolite material is shown in Fig. 9. These catalysts are supported on a ceramic honeycomb.

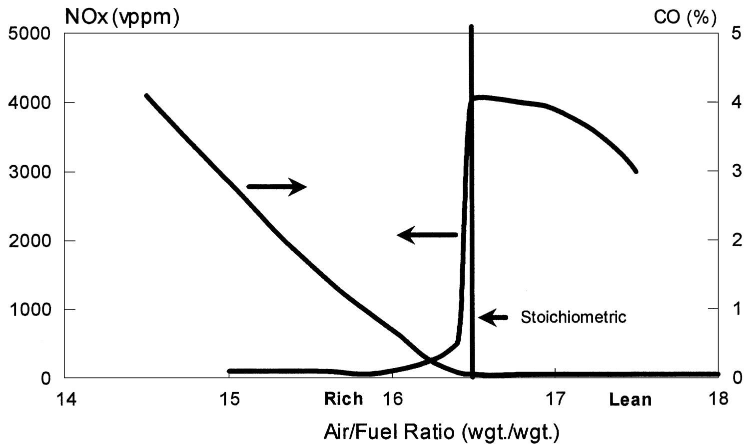

Fig. 8. Emissions from a natural gas stationary engine using NSCR NO_x. From Catalytic Air Pollution Control: Commercial Technology [3].

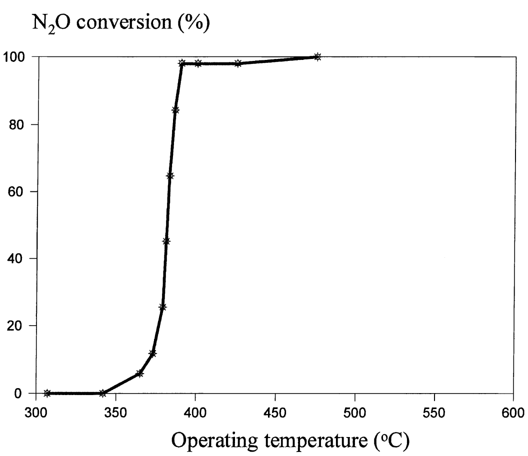

Fig. 9. N_2O decomposition over Co/Beta zeolite.

4. Conclusions

Catalyst technology is commercially available for selective NO_x reduction using V_2O_5/TiO_2 catalysts with modifiers, and this same technology can be adapted to mobile applications. NO_x reduction for stationary engines and nitric plants can use either SCR or NSCR technology for reducing NO_x emissions. N_2O decomposition catalyst is available for application to reduce N_2O emissions in nylon plants. Catalytic abatement of nitrogen oxides for stationary applications has become a mature technology and the new advancements will be mainly in engineering design and mobile applications.

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